(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : **0 595 053 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number : **93115796.0**

(22) Date of filing : **30.09.93**

(51) Int. Cl.[5] : **C23F 1/18**, C23F 1/02, C23F 4/00, H01L 21/321

(30) Priority : **30.10.92 US 954131**

(43) Date of publication of application : **04.05.94 Bulletin 94/18**

(84) Designated Contracting States : **DE FR GB IT NL**

(71) Applicant : **TEXAS INSTRUMENTS INCORPORATED**
13500 North Central Expressway
Dallas Texas 75265 (US)

(72) Inventor : **Douglas, Monte A.**
627 Hood Drive
Coppell, TX 75019 (US)

(74) Representative : **Bunke, Holger, Dr.rer.nat. Dipl.-Chem. et al**
Prinz & Partner Manzingerweg 7
D-81241 München (DE)

(54) Anisotropic liquid phase photochemical etch method.

(57) An anisotropic liquid phase photochemical etch is performed by a substrate **30** (e.g. copper) in a liquid **34** containing all etchant (e.g. hydrochloric acid) and a passivant (e.g. iodine), the passivant forming an insoluble passivation layer **36** (e.g. CuI) on the surface, preventing the etchant from etching the surface. The passivant and its concentration are chosen such that the passivation layer **36** has a solubility which is substantially increased when it is illuminated with radiation **38** (e.g. visible/ultraviolet light). Portions of the surface are then illuminated with radiation 88, whereby the passivation layer **36** is removed from these illuminated portions of the surface, allowing the etch to proceed there. Portions of the surface not illuminated are not etched, resulting in an anisotropic etch. Preferably, an etch mask **32** is used to create the inilluminated areas. This etch mask **32** may be formed on the surface or it may be interposed between the surface and the radiation source.

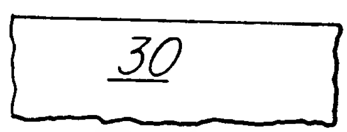

Fig.1

EP 0 595 053 A2

Jouve, 18, rue Saint-Denis, 75001 PARIS

Field of the Invention

This invention generally relates to the fabrication of integrated circuits, and particularly etch process technology.

Background of the Invention

Without limiting the scope of the invention, its background is described in connection with current anisotropic etch techniques.

The fabrication of modern integrated circuits often requires the patterning of materials to very small dimensions and verg stringent tolerances. At some stage of virtually any process of manufacturing integrated circuits discrete devices, many materials including crystalline and non-crystalline semiconductors, insulators and metals must be formed in very precise patterns. A common technique is to deposit a continuous film of the required material, then form an etch mask on the surface of the material (commonly a photoresist layer which has been patterned with a photolithographic technique), and then to etch away the portions of the film not covered by the etch mask, leaving the desired pattern.

Clearly, an etch technique should not etch away material under the etch mask if the pattern defined by the mask is to be preserved in the underlying material. Any etch for this purpose should therefore be largely directional (anisotropic). The desired etch direction is usually normal to the surface of the substrate (i,e. the etch proceeds down into the underlying material but not laterally underneath the mask), An anisotropic etch will ideally leave a virtually vertical sidewall under the etch mask edge.

Plasma etches are among the dry etches which are widely used and are made anisotropic largely by the direction of the applied electric field. Liquid phase chemical etches (wet etches) are generally assumed to be nondirectionel (isotropic), and therefore have not found widespread use in the manufacture of VLSI devices. While wet etches are desirable because they are generally low energy techniques which cause little or no damage to substrate materals, unfortunately only a few anisotropic wet etches are known. Crystalline silicon, for example, may be anisotropically etched to some degree with potassium hydroxide. Some chlorine reagents will directionally etch gallium arsenide. These orientation dependent etch (hereafter referred to as ODE) methods are anisotropic because the etch rate along one crystal orientation is faster than that of other directions.

Summary of the Invention

The few known anisotropic wet etches are not widely applicable to integrated circuit manufacturing for several reasons. First, orientation dependent etches are known for only a few materials used in integrated circuit manufacture. In addition, the direction of an ODE is not necessarily the desired direction (typically normal to the substrate surface). Orientation dependent etches are clearly only anisotropic for crystalline materials. In addition, this type of directional etching results in very sharp corners between the facets defined by the different crystalline orientations. The sharp corners can cause extremely high electric fields and/or dislocations during oxidation, for example, which make these etches unacceptable for state-of-the-art semiconductor processing.

Plasma etches are often not suitable because they are generally high energy techniques. For example, the high electric fields, temperatures and kinetic energies associated with these etches can cause unacceptable material damage and device performance degradation.

Current etch techniques present a tradeoff between high energy anisotropic etches (e.g. plasma etching) and low energy isotropic wet etches, The present invention overcomes this tradeoff by providing an anisotropic liquid phase etch which is generally applicable to a wide variety of materials (single crystal, poly-crystalline and non-crystalline), is low energy, and which is easily integrated into current processes for integrated circuit manufacture.

Generally, and in one form of invention, an anisotropic liquid phase photochemical etch is performed by submersing a surface in a liquid etchant, then adding a passivant to the liquid etchant which forms an insoluble passivation layer on the surface, preventing the etchant from relatively rapidly etching the surface. The passivant and its concentration are chosen such that the passivation layer has a solubility which is substantially increased when it is illuminated with radiation (e.g. visible light). Portions of the surface are then illuminated, whereby the passivation layer is removed from those illuminated portions of the surface, allowing the etch to proceed there. Portions of the surface not illuminated are substantially not etched, resulting in an anisotropic etch. Preferably, an etch mask is used to create the unilluminated areas. This etch mask may be formed on the surface or it may be interposed between the surface and the radiation source.

This is a method to allow anisotropic liquid phase etching which is independent of the crystalline structure

of the substrate. The advantages of this method are many. It allows anisotropic etching of amorphous, polycrystalline and single crystal materials. The etch direction may be made normal to the substrate surface regardless the crystal orientation (if any) of the substrate. It can be used on all single crystal materials whereas known ODE techniques are limited to only a few materials. It does not generate the sharp corners characteristic of ODE that cause high field and dislocation problems. Compared to dry etching, it is virtually a damage-free process, which is a growing need for current and next generation semiconductor devices. In addition, the process offers a capability to directionally etch a much broader spectrum of materials compared to dry etching which depends, primarily, on the volatility of halogen compounds.

Brief Descriptions of the Drawings

The novel features believed characteristic of the invention are set forth in the appended claims. The invention itself, however, as well as other features and advantages thereof, will be best understood by reference to the detailed description which follows, read in conjunction with the accompanying drawings.

In the drawings:

FIGURES 1-4 are microscopic cross sections of a substrate undergoing liquid phase photochemical etching which depict the function of etch passivation when the etch mask is in contact with the substrate.

FICURES 5-8 are microscopic cross sections of a substrate undergoing liquid phase photochemical etching which depict the function of etch passivation when the etch mask is displaced from the substrate.

Detailed Description of the Preferred Embodiments

A first preferred embodiment of this invention is described with reference to Figures 1, 2, 3 and 4, which illustrate anisotropic liquid phase etching where the etch mask is in contact with the substrate to be etched Figure 1 shows a greatly magnified cross section of a substrate **30**. Figure 2 shows the surface of the substrate partially covered with an etch mask **32**. This etch mask may be formed of photoresist by standard photolithographic techniques, or may be any material which is etch resistant (and preferably opaque to the illuminating radiation) and which adheres to the surface. Figure 3 depicts the substrate and etch mask immersed in a liquid **34**. The liquid contains one or more etchants and one or more passivants. A passivant is chosen such that it causes the formation of a thin insoluble passivation layer **36** to form on the exposed surface of the substrate. This layer is typically extremely thin (possibly a monolayer); its thickness is greatly exaggerated in the figures for clarity. This insoluble layer prevents the etchant from etching the substrate. Upon illumination with radiation **38**, as depicted in Figure 4, the passivation layer **36** is removed from the substrate **30** and etching proceeds in areas which are illuminated. A substantially vertical sidewall **40** forms, which is protected from etching by the vertical passivation layer **42**. This vertical passivation layer **42** is not removed from the sidewall **40** because it is in the shadow of the etch mask **32**.

A second preferred embodiment of this invention is described with reference to Figures 5, 6, 7 and 8 which illustrate anisotropic liquid phase etching where the etch mask is displaced from the substrate to be etched. Figure 5 shows a greatly magnified cross section of a substrate **30**. Figure 6 shows the surface of the substrate immersed in a liquid **34**. Again, the liquid containg one or more etchants and one or more passivants. A passivant is chosen so that it causes the formation of a thin insoluble passivation layer **36**. This layer is again typically extremely thin (possibly a monolayer) with its thickness greatly exaggerated in the figures for clarity. This insoluble layer substantially prevents the etchant(s) from etching the substrate. As shown in Figure 7, an etch mask **32** is positioned above the substrate **30** so that it blocks the radiation **38** at selected portions of the substrate. This etch mask may be any material which is sufficiently opaque to the illuminating radiation, and is not necessarily positioned within the liquid. Upon illumination with radiation, as depicted in Figure 8, the insoluble passivation layer **36** is removed from the substrate **30** in those areas where the radiation is not blocked by the etch mask **32**. With the passivation layer removed, etching of the substrate proceeds in those illuminated areas. Again, a substantially vertical sidewall **40** forms, which is protected from etching by the vertical passivation layer **42**. This vertical passivation layer **42** is not removed from the sidewall **40** because it is in the shadow of the etch mask **32**.

In both preferred embodiments, an etchant is chosen which will etch the substrate (in the absence of a passivation layer) with or without the presence of the illuminating radiation. The passivant is chosen to form a layer on the substrate surface which is removed or partially removed by radiation. Although the mechanism or explanation for this removal is uncertain, it is thought that the passivant bonds to the surface under no illumination, but is detached from the surface and re-enters solution when illuminated.

An important aspect of this invention is the automatic passivation of sidewalls as they are formed. As depicted in the figures, sidewalls are created when illuminated areas are removed by etching. The sidewalls are

etched only to the point where they are in the shadow of the etch mask The passivation layer then remains on the vertical surface and the sidewall is protected from further etching. Very high etch anisotropy is achieved.

It should be noted that the etch rate of some liquid etches may be accelerated by illuminating radiation, thereby exhibiting some anisotropy without passivation. The technique set forth in the instant preferred embodiments may be used with these photochemical wet etches to further enhance their anisotropy (i.e. increase the ratio of illuminated etch rate to unilluminated etch rate). Passivation of the wall occurs as the etching proceeds.

The conditions of the etch process may be changed to affect, for example, the illuminated etch rate and the illuminated/unilluminated etch rate ratio. The temperature of the liquid may be changed. The concentration of both the etchant and passivant may of course be varied. The liquid may be made to flow with respect to the substrate. The intensity and wavelength of the radiation may be varied. The illuminating radiation need not be constant in time, i e. the radition source may be pulsed.

In an experiment to demonstrate this technique, copper was anisotropically etched in a liquid containing 0.1 % molar concentration hydrochloric acid (the etchant) and 0.019 % molar iodine (the passivant). A layer of copper was deposited on a crystalline silicon substrate, and a photoresist etch mask was then formed on the copper. The illuminating radiation was provided by a 200 Watt mercury/xenon lamp, which produces visible(ultraviolet radiation. When the lamp was switched on, the etch proceeded in those areas not covered by photoresist until no copper remained. Essentially no undercut of the photoresist occurred. The same experiment performed with no iodine present in the liquid resulted in severe undercut of the etch mask.

In another example of this technique, mercury cadmium telluride (hereafter referred to as MCT) was anisotropically etched in a liquid containing 0.1 % molar concentration hydrochloric acid (the etchant) and 0.1 % molar concentration iodic acid (the passivant). The illuminating radiation was again provided by a 200 Watt mercury/xenon lamp. Anisotropic etching of the MCT was achieved.

The sole Table, below, provides an overview of some embodiments and the drawings.

TABLE

Figure Element	General Term	Specific or Preferred Term	Alternate Terms/Function
30	Substrate	Copper	
32	Etch Mask	Photoresist	Blocks radiation
34	Liquid	0.1 % molar HCl and 0.019 % molar I_2	Contains etchant and passivant
	Etchant	0.1 % molar HCl	Etches substrate with or without presence of illuminating radiation in absence of passivation layer.
	Passivant	0.019 molar I_2	Reacts with substrate to form passivation layer.
36	Passivation layer	CuI, CuI_2	Product of passivant and substrate; removed from surface by radiation.
38	Radiation	Visible/UV light from 200 Watt mercury/xenon lamp	Removes or partially removes passivation layer from surface
40	Sidewall		Forms as etch proceeds in illuminated areas
42	Sidewall passivation layer	CuI,CuI_2	Forms on sidewall under edge of etch mask as etch proceeds; remains because sidewall is in shadow

A few preferred embodiments have been described in detail hereinabove. It is to be understood that the scope of the invention also comprehends embodiments different from those described, yet within the scope of the claims. Various modifications and combinations of the illustrative embodiments, as well as other embodiments of the invention, will be apparent to persons skilled in the art upon reference to the description. The "substrate" may consist, for example, of partially fabricated electronic circuitry. The liquid may be acidic, neutral or basic. Salt solutions are contemplated, well as solutions containing organic solvents. Pure water may be used as an etchant. Use of this technique is contemplated for the manufacture of discrete components or fully integrated circuits in silicon, gallium arsenide, or other electronic materials families, as well as in optical-based or other technology-based forms and embodiments. It is therefore intended that the appended claims encompass any such modifications or embodiments.

Claims

1. An anisotropic etch method comprising:
   submersing a surface of a substrate in a liquid, said liquid including at least one etching agent;
   adding a passivation agent to said liquid, said passivation agent fbrming a passivation layer on said surface and being substantially insoluble in said liquid; and
   irradiating portions of said surface with radiation to produce irradiated areas and substantially non-irradiated areas, thereby causing the passivation layer to be substantially removed from said irradiated areas.

2. The method according to Claim 1, wherein said step of adding passivation agent comprises adding the agent to said liquid before said surface if submersed

3. The method according to Claim 1 or Claim 2, wherein the etching occurs at a rate which is substantially unchanged by said irradiation.

4. The method according to any preceding Claim, further comprising causing said liquid to flow with respect to said surface.

5. The method according to any preceding Claim, further comprising modulating the intensity of said radiation with time.

6. The method according to any preceding Claim, further comprising changing the intensity of said radiation such that it is not equal at all points on said surface.

7. The method according to any preceding Claim, further comprising maintaining the temperature of said liquid to be approximately 25 °C.

8. The method according to any preceding Claim, further comprising irradiating said surface with monochromatic radiation.

9. The method according to any preceding Claim, further comprising providing said etching agent as H_2O.

10. The method according to any of Claims 1 to 8, further comprising providing said surface as copper; said etching agent as hydrochloric acid in 0.1 % molar concentration; and said passivation agent as iodine in 0.019 % molar concentration.

11. The method of Claim 10, further comprising:
    submersing said copper in the 0.1 % molar hydrochloric acid containing the 0.019 % molar iodine; and
    illuminating said copper with visible/ultraviolet radiation produced by a 200 Watt mercury/xenon lamp.

12. The method according to Claim 11, further comprising providing said copper on a crystalline silicon substrate.

13. The method of Claim 9, further comprising submersing said surface in an aqueous solution, said aqueous solution including at least one said etchant.

14. The method according to Claim is, further comprising providing said aqueous solution having greater than 90% H_2O.

15. An integrated circuit fabricated by the method of any preceding Claim.

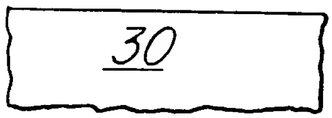

Fig.1

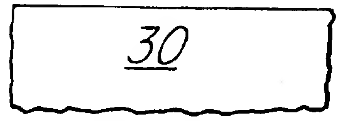

Fig.5

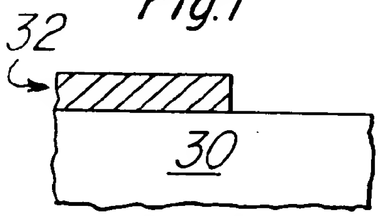

Fig.2

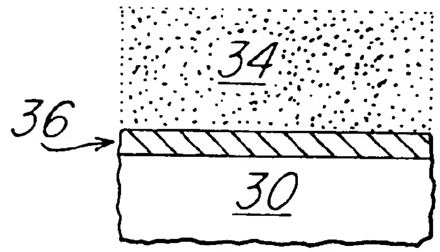

Fig.6

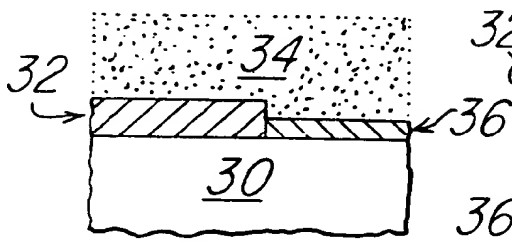

Fig.3

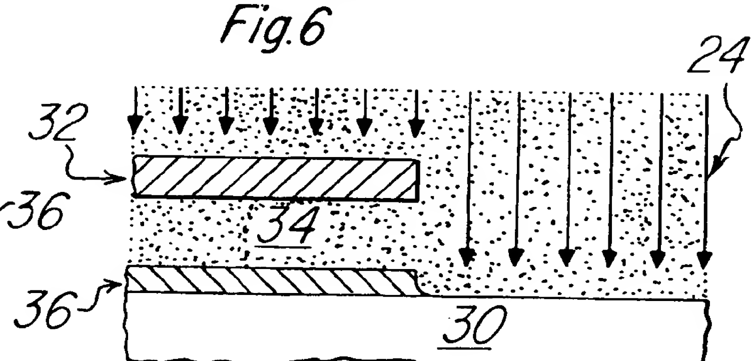

Fig.7

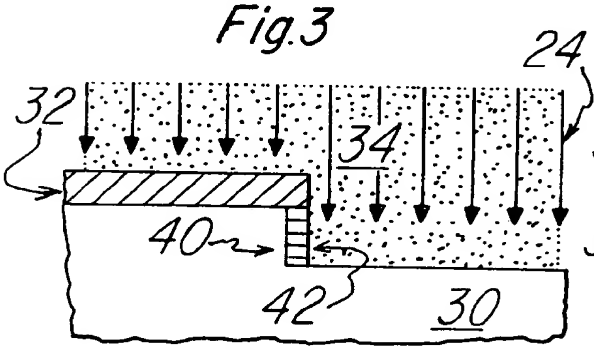

Fig.4

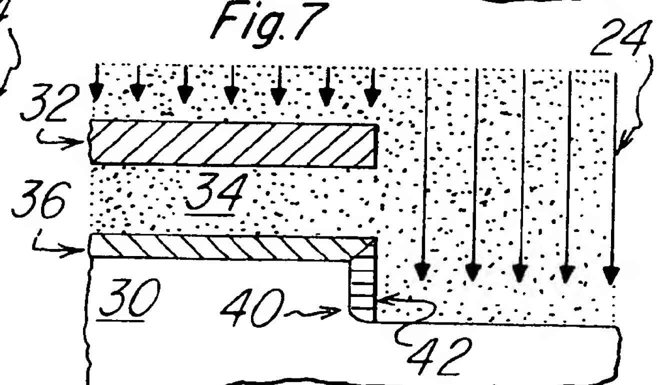

Fig.8

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : **0 595 053 A3**

(12) EUROPEAN PATENT APPLICATION

(21) Application number : **93115796.0**

(22) Date of filing : **30.09.93**

(51) Int. Cl.[5] : **H01L 21/321,** C23F 1/02, C23F 1/18, C23F 4/00, H05K 3/06

(30) Priority : **30.10.92 US 954131**

(43) Date of publication of application : **04.05.94 Bulletin 94/18**

(84) Designated Contracting States : **DE FR GB IT NL**

(88) Date of deferred publication of search report : **22.03.95 Bulletin 95/12**

(71) Applicant : **TEXAS INSTRUMENTS INCORPORATED**
13500 North Central Expressway
Dallas Texas 75265 (US)

(72) Inventor : **Douglas, Monte A.**
627 Hood Drive
Coppell, TX 75019 (US)

(74) Representative : **Bunke, Holger, Dr.rer.nat. Dipl.-Chem. et al**
Prinz & Partner
Manzingerweg 7
D-81241 München (DE)

(54) Anisotropic liquid phase photochemical etch method.

(57) An anisotropic liquid phase photochemical etch is performed by a substrate **30** (e.g. copper) in a liquid **34** containing all etchant (e.g. hydrochloric acid) and a passivant (e.g. iodine), the passivant forming an insoluble passivation layer **36** (e.g. CuI) on the surface, preventing the etchant from etching the surface. The passivant and its concentration are chosen such that the passivation layer **36** has a solubility which is substantially increased when it is illuminated with radiation **38** (e.g. visible/ultraviolet light). Portions of the surface are then illuminated with radiation 88, whereby the passivation layer **36** is removed from these illuminated portions of the surface, allowing the etch to proceed there. Portions of the surface not illuminated are not etched, resulting in an anisotropic etch. Preferably, an etch mask **32** is used to create the inilluminated areas. This etch mask **32** may be formed on the surface or it may be interposed between the surface and the radiation source.

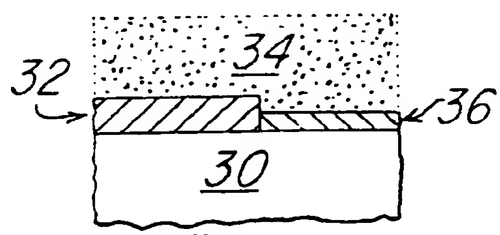

Fig.3

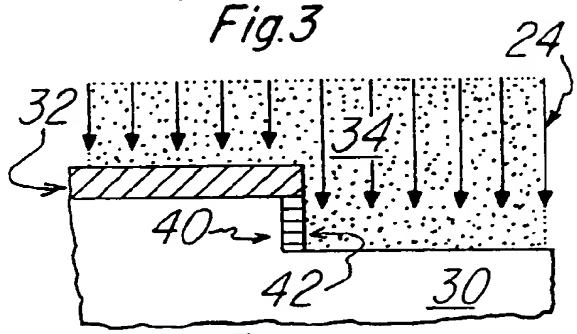

Fig.4

Jouve, 18, rue Saint-Denis, 75001 PARIS

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 11 5796

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	US-A-3 489 564 (DONALD N. SCHAEFER) * column 1, line 10 - line 26; claim 1 * * column 2, line 15 - line 71 *	1,2,8	H01L21/321 C23F1/02 C23F1/18 C23F4/00 H05K3/06
Y		4-6	
A		9,13	
Y	US-A-4 838 989 (CAROL I.H. ASHBY ET AL.) * column 2, line 43 - line 68 * * column 3, line 28 - line 55 * * column 4, line 31 - line 41 * * column 4, line 51 - column 5, line 8 *	5,6	
A		1	
Y	ELECTRONIC PACKAGING AND PRODUCTION, vol.30, no.8, August 1990, MASSACHUSETTS US pages 58 - 61 JOE FJELSTAD 'Etching fine line Printed Circuit Boards' * page 60, right column *	4	
P,X	US-A-5 201 989 (MONTE A. DOUGLAS ET AL.) * column 2, line 1 - line 26 * * column 2, line 41 - column 3, line 2 * * column 3, line 13 - line 35 * * column 3, line 41 - line 44 * * column 3, line 45 - line 47 * * column 3, line 50 - line 53 *	1,4,5,7,8,15	TECHNICAL FIELDS SEARCHED (Int.Cl.5) H01L C23F C23G H05K C03C

-/--

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	2 January 1995	Klopfenstein, P

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 11 5796

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A	US-A-3 762 325 (ROBERT W. HALLMAN ET AL.) * column 1, line 41 - line 67 * * column 2, line 30 - column 3, line 2; figure 1 * * column 3, line 12 - line 37 * * column 4, line 35 - line 65 * * column 5, line 27 - line 48 * * column 6, line 30 - line 55; figures 2-4 * ---	1-3,8, 10,11,13	
A	US-A-4 861 421 (RACHELLE J. BIENSTOCK) * column 2, line 19 - line 34 * * column 2, line 54 - column 3, line 33; figure 1 * * column 3, line 60 - column 4, line 2 * ---	1,2,9	
A	EP-A-0 433 983 (TEXAS INSTRUMENTS INC.) * column 3, line 12 - line 28 * * column 4, line 11 - column 5, line 17; figure 1 * * column 5, line 45 - column 6, line 40; figures 2A,2B * ---	1	TECHNICAL FIELDS SEARCHED (Int.Cl.5)
P,A	EP-A-0 520 437 (ORBOT SYSTEMS LIMITED) * column 2, line 52 - column 3, line 7 * * column 3, line 42 - column 4, line 25; figures 1A-1E * * column 4, line 34 - line 38 * * column 5, line 56 - column 6, line 26; claims 1,4,5,8,9; figures 3A-3E * -----	1,8,10, 15	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	2 January 1995	Klopfenstein, P

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)